Lecture topics

(1) Class exercise: work out by qualitative reasoning how $U=U(T)$, $C_V=C_V(T)$ given qualitative dependence of entropy curve $S=S(U)$ for paramagnetic

(2) Complete derivation of multiplicity $S(U,V,N)$ for monatomic ideal gas

(3) Discuss implications of formula $S(U,V,N)$ for ideal gas
   
   - $S(U,V,N)$ very sharply peaked about equal value
   - Sachur-Tetradec equation $S=S(U,V,N)$
   - Entropy change for isothermal process implicit $\Delta S = \frac{Q}{T}$
   - Entropy of mixing, Gibb's paradox

(4) Measuring entropy experimentally via heat capacities

(5) Third law of thermodynamics: $S(T=0)=0 \Rightarrow C_V, C_p \to 0$ as $T \to 0$
Class exercise: deducing qualitative insight

\( U = U(t) \), \( C = C(t) \) from given entropy curve \( S = S(U) \)

Assume

Deduce:

(a)

\( \frac{1}{T} = \frac{dS}{dT} \)

(b)

(c)

For this last curve, use fact we show later that

\( C_v(t) \to 0 \) as \( t \to \infty \)
Back to discussion of $S(U, V, N)$ for monoatomic gas of $N$ identical atoms in isolated volume $V$, with fixed total energy $U$.

**Macrostate**: given values of $U, V, N$

**Microstate**: $6N$ numbers consisting of position, momentum

$$\{ x_i, y_i, z_i, px_i, py_i, pz_i \}_{i=1}^N$$

momentum more fundamental than velocity since $p$ but not $\nabla$ shows up in quantum mechanics.

Reason heuristically to estimate $S_2$; guess how it may depend on various quantities.

Consider case for $N=1$, one atom.

Center of mass $(x, y, z)$ can be anywhere in volume, and bigger volume implies more locations, so guess

$$S_2(U, V, N=1) \propto V$$

Energy conservation implies

$$U = \frac{p^2}{2m} = \frac{1}{2m} (px^2 + py^2 + pz^2)$$

or

$$px^2 + py^2 + pz^2 = \left( \frac{2U}{m} \right)^2$$

$(px, py, pz)$ lie on surface of sphere of radius $r = \sqrt{2mU}$.
Guess that multiplicity $S_L$ proportional to possible ways we can vary $\vec{p}$ on surface of sphere, i.e., to surface area $A_3(r) = \text{area of 3D sphere of radius } r = \sqrt{3} \pi r^2$.

$$S_L(\bar{y}, y, N = 1) \propto \sqrt{A_3(r)}$$

This looks implausible, right side is finite but clearly, volume $V$ and area $A_3(r=\tau M)$ correspond to continuum of possible positions $\vec{x}$ and momenta $\vec{p}$, so $S_L$ should be infinite.

One way out is to assume finite experimental resolution, $\Delta x$, $\Delta p$, when measuring location and momentum, but this makes $S_L$ depend in unsatisfying way on arbitrary resolution.

Quantum mechanics gives definitive resolution of how to obtain finite value of $S_L(y, y, N)$ when microstates can vary continuously. Justification too complicated to explain at level of this course, requires Physics 211 discussion of the so-called "semiclassical" limit of QM as to become small, use WKB perturbation theory. So let's just assume result of this analysis.
Semi-classical limit of quantum mechanics says that uncertainty principle

\[ \Delta x \Delta p_x \geq h \]
\[ \Delta y \Delta p_y \geq h \]
\[ \Delta z \Delta p_z \geq h \]

leads to a quantization of "phase space" or "state space" the space consisting of points \((x, y, z, p_x, p_y, p_z)\) that give state of single particle.

Multiplying the above 3 inequalities gives

\[
\frac{dx \, dy \, dz \cdot dp_x \, dp_y \, dp_z}{h^3} \geq \frac{1}{h^3}
\]

i.e. we can think of phase space as broken up into little 6-dimensional cubes of size \(h^3\)

\[
S(\Delta x, \Delta y, \Delta z) = \sum \sum \sum \sum \frac{dx \, dy \, dz \cdot dp_x \, dp_y \, dp_z}{h^3}
\]

The integrals over \(dx, dy, dz\) lead to volume \(L_x L_y L_z = V\)

Integrals over \(dp_x, dp_y, dp_z\) more complicated because the triple integrals are constrained, they go over surface of sphere \(p_x^2 + p_y^2 + p_z^2 = 2mU\) but they end up being proportional to \(A_3(\sqrt{2mU})\)
Result of previous conclusion:

\[ S^2(U, V, N=1) = \frac{VA_3(\frac{12\mu}{h^3})}{h^3} \]

giving precise and correct multiplicity

**Case \( N = 2 \)**

Position \( \vec{X}_1 \) of particle 1 independent of \( \vec{X}_2 \) so gives

\[ S^2(U, V, N=2) \propto V^2 \]

Momentum \( \vec{P}_1 \) of particle 1 is not independent of \( \vec{P}_2 \) because

For isolated system

\[ U = \frac{\vec{P}_1^2}{2m} + \frac{\vec{P}_2^2}{2m} = \frac{1}{2m} \left[ P_{1x}^2 + P_{1y}^2 + P_{1z}^2 + P_{2x}^2 + P_{2y}^2 + P_{2z}^2 + \delta^2 \right] \]

or

\[ P_{1x}^2 + P_{1y}^2 + P_{1z}^2 + P_{2x}^2 + P_{2y}^2 + P_{2z}^2 = (\sqrt{2mU})^2 \]

This is surface of 6-dimensional hypersphere. Conclude

\[ S^2(U, V, N=2) = \frac{V^2 A_6(\frac{12\mu}{h^3})}{(h^3)^2} X \]

Notice we need twice as many h's to count cubes in big phase space.
Implications of Identical Particles For $S_2(Y,Y,N)$

Conclusion: $S_2(Y,Y,N=2) = \frac{V^2 A_6(Y_{2nu})}{(\hbar^3)^2}$ is wrong.

For identical atoms, it overcounts the microstates by including microstates with two particles exchanged $(x_i, p_i) \leftrightarrow (x_j, p_j)$.

Correct formula is

$$S_2(Y,Y,N=2) = \frac{V^2 A_6(Y_{2nu})}{(\hbar^3)^2} \frac{1}{2!}$$

General case is then

$$S_2(Y,Y,N) = \frac{1}{N!} \frac{V^N A_{3N}(Y_{2nu})}{h^{3N}} \left( \frac{1}{h^3} \right)^N$$

Note: the particles like $e$, $\nu$, $\bar{\nu}$ truly exactly identical, no hidden labels.

Answer is yes, this is prediction of quantum field theory.

Feynman's crazy idea: only one electron in universe, travels back in time to interact with itself, would explain why all particles exactly identical.
Class project: what is $S_2(y, L, N)$ for ideal gas on one-dimensional carbon nanotube of length $L$?

\[ S_2(y, L, N) = \frac{L^2 A(\zeta)}{h^2} x^2 \]

\[ \zeta \approx 0.3 \text{ nm} \]
Surface area of d-dimensional hypersphere of radius $r$

There is an analytical formula

$$A_d(H) = \frac{2 \cdot \pi^{d/2} \cdot r^{d-1}}{\Gamma\left(\frac{d}{2}\right)}$$

where $\Gamma(x)$ is Euler Gamma function.

Some values:

$$A_2(1) = \frac{2 \cdot \pi^{1/2}}{\Gamma\left(\frac{3}{2}\right)} = 2\pi^1$$

$$A_3(1) = \frac{2 \cdot \pi^{3/2}}{\Gamma\left(\frac{5}{2}\right)} = \frac{3}{2} \pi^2$$

In homework, you calculate $A_4(1)$, $A_5(1)$, plot $A_d(r)$ vs $d$.

Outline of derivation:

$$\int_{-\infty}^{\infty} e^{-x^2} \, dx \times \int_{-\infty}^{\infty} e^{-x^2} \, dx \times \cdots \times \int_{-\infty}^{\infty} e^{-x^2} \, dx \, dx = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-(x_1^2 + x_2^2 + \cdots + x_d^2)} \, dx_1 \cdots dx_d$$

$$\pi^{d/2} = \int_0^\infty \frac{e^{-r^2}}{r^{d-1}} \, dr = A_d(1) \int_0^\infty e^{-r^2} \, dr$$

(change variable $t = r^2$ to express in terms of $\Gamma$)
Paradox: high-dimensional volume
are mainly surface

Consider d-dimensional hypercube of length 1, volume
\[ V_d = 1 \times 1 \times \ldots \times 1 = 1 \]

Consider concentric smaller hypercube, of side 1-2\( \epsilon \)

\[ V = (1-2\epsilon) \times (1-2\epsilon) \times \ldots \times (1-2\epsilon) = (1-2\epsilon)^d \]

\[ (0.99)^{10^3} \approx 0.1 \quad \Rightarrow \quad 60\% \ of \ volume \ of \ unit \ hypercube \ lies \ within \ 0.005 \ of \ surface! \]

\[ (0.99)^{10^3} \approx 0.1 \quad \Rightarrow \quad cube \ is \ all \ surface \]
Formula For Multiplicity

\[ S(N, l, v, N) = \frac{1}{N!} \cdot \frac{\sqrt{N}}{h^{3N}} \cdot \frac{1}{\sqrt[3]{(\frac{2\pi m l}{\hbar^2})^{3N/2}}} \cdot (\frac{2\pi m l}{\hbar^2})^{3N-1} \]

For N large, can simplify:

\[ \Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2} - 1\right)! \approx \left(\frac{3N}{2}\right)! \quad \text{for} \quad N \gg 1 \]

\[ S(N, l, v, N) \approx f(N) \cdot V^N \cdot U \]

\[ f(N) = \left(\frac{2\pi m l}{\hbar^2}\right)^{3N/2} \frac{1}{N! \left(\frac{3N}{2}\right)!} \]

\[ S = k \ln S \approx k \ln \left(\frac{2\pi m l}{\hbar^2}\right)^{3N/2} \cdot \frac{1}{N! \left(\frac{3N}{2}\right)!} \cdot V^N \]

\[ = k \left[ N \ln N + N \ln \left(\frac{2\pi m l}{\hbar^2}\right)^{3N/2} - N \ln N - \frac{3N}{2} \ln \left(\frac{3N}{2}\right) + \frac{3N}{2} \right] \]

\[ S \approx Nk \left[ \frac{5}{2} + \ln\left(\frac{\sqrt{V} \left(\frac{4\pi m l}{\hbar^2}\right)^{3N/2}}{N}ight) \right] \quad \text{ideal gas} \]

\[ \approx 1912 \]

Sackur-Tetrode equation for entropy of monoatomic gas